

# **MARKET OUTLOOK FOR DIMETHYL ETHER (DME)**

## **TOPICAL REPORT**

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**for the  
Air Products Liquid Phase Conversion Company, L.P.**

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## **Abstract**

The Liquid Phase Methanol (LPMEOH™) Demonstration Project at Kingsport, Tennessee, is a \$213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L.P. (the Partnership) to produce methanol from coal-derived synthesis gas (syngas). Syngas is a mixture of primarily hydrogen and carbon monoxide. Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project.

This project has also been evaluating the demonstration of the production of dimethyl ether (DME) as a mixed coproduct with methanol using Air Products' Liquid Phase Dimethyl Ether (LPDME) Process. In 1999, a demonstration of the LPDME Process was successfully completed in a slurry bubble column reactor at the DOE's Alternative Fuels Development Unit (AFDU) in LaPorte, Texas. The demonstration was conducted at pilot-scale of 10 short tons per day (sT/D) to evaluate the commercial viability of the LPDME Process. Syngas produced from coal as well as natural gas can be converted to form DME as a mixed coproduct with methanol.

This Topical Report provides data on the status of the current market for DME and an outlook on potential market developments through 2006. Over 50% of the demand for DME worldwide (currently between 100,000 and 150,000 metric tons per year) is for use as a projectile agent. DME is also being used as a methylating agent, and as a cleaning material for laboratory systems and some high precision, high value added applications, such as in electronics.

DME has potential applications as a chemical building block. In addition, since the characteristics of DME are similar to those of liquefied petroleum gas (LPG) and given its higher heating value, it has been speculated that DME could be used in large scale power production, in home heating, in replacement of LPG for automobiles, and as a diesel fuel substitute or combustion supplement. In these applications, the specification for the purity of DME has been reported to lower than the 99 weight percent (wt%) requirement for current uses, which may provide an opportunity for savings in capital and operating costs for product distillation. If these markets are developed, production capacity for DME will need to increase by an order of magnitude over current levels of about 143,000 metric tons per year. Projects to meet this future market are under development, including two large natural gas-based opportunities serving markets in India and Japan and a coal-based opportunity in China.

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## ACRONYMS AND DEFINITIONS

**Term:**

**Definition:**

Air Products	Air Products and Chemicals, Inc.
AFDU	Alternative Fuels Development Unit - The “LaPorte PDU”
CCT	Clean Coal Technology
CN	cetane number
Btu	British Thermal Unit
DME	dimethyl ether
DOE	United States Department of Energy
DVT	Design Verification Testing
Eastman	Eastman Chemical Company
IDA	International DME Association
IGCC	Integrated Gasification Combined Cycle, a type of electric power generation plant.
LPDME	Liquid Phase Dimethyl Ether
LPG	liquefied petroleum gas
LPMEOH™	Liquid Phase Methanol
Partnership	Air Products Liquid Phase Conversion Company, L.P.
sT/D	short ton(s) per day
Syngas	Abbreviation for Synthesis Gas
Synthesis Gas	A gas containing primarily hydrogen (H <sub>2</sub> ), carbon monoxide (CO), or mixtures of H <sub>2</sub> and CO; intended for “synthesis” in a reactor to form methanol and/or other hydrocarbon products (Synthesis gas may also contain carbon dioxide (CO <sub>2</sub> ), water, and other gases)
wt%	weight percent

## **Executive Summary**

The Liquid Phase Methanol (LPMEOH™) Demonstration Project at Kingsport, Tennessee, is a \$213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L.P. (the Partnership) to produce methanol from coal-derived synthesis gas (syngas). Syngas is a mixture of primarily hydrogen and carbon monoxide. Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project. The LPMEOH™ Process Demonstration Unit was designed, constructed, and is in operation at a site located at the Eastman chemicals-from-coal complex in Kingsport.

The project involves the operation of an 80,000 gallons per day (260 short tons per day (sT/D)) methanol unit utilizing coal-derived syngas from Eastman's integrated coal gasification facility. The new equipment consists of syngas feed preparation and compression facilities, the liquid phase reactor and auxiliaries, product distillation facilities, and utilities.

This project has also been evaluating the demonstration of the production of dimethyl ether (DME) as a mixed coproduct with methanol using Air Products' Liquid Phase Dimethyl Ether (LPDME) Process. In 1999, a demonstration of the LPDME Process was successfully completed in a slurry bubble column reactor at the DOE's Alternative Fuels Development Unit (AFDU) in LaPorte, Texas. The demonstration was conducted at pilot-scale of 10 sT/D to evaluate the commercial viability of the LPDME Process. Syngas produced from coal as well as natural gas can be converted to form DME as a mixed coproduct with methanol.

This Topical Report provides data on the status of the current market for DME and an outlook on potential market developments through 2006. DME is a colorless and combustible gas at ambient temperature and pressure. DME has physical properties that are similar to liquefied petroleum gas (LPG), and can be stored and transported as a liquid product in pressurized vessels.

The most important application for DME today is as an aerosol propellant. Over 50% of the demand for DME worldwide (currently between 100,000 and 150,000 metric tons per year) is for this application. DME is also being used as a cleaning material for laboratory systems and some high precision, high value added cleaning applications, such as in electronics. The balance of DME demand is for use as a methylating agent and for miscellaneous experimental work.

DME is sold and marketed similarly to LPG. DME is sold by the major producers on a wholesale basis to major users, who store and use the chemical on site. Over 30% of the DME that is marketed in the United States is sold through distributors, who supply small quantities of DME in either high pressure gaseous cylinders or lower pressure liquid containers to small volume users.

DME has potential applications as a chemical building block. In addition, since the characteristics of DME are similar to those of LPG and given its higher heating value, it has been speculated that DME could be used in large scale power production, in home heating, in

replacement of LPG for clean combustion automobiles, and as a diesel fuel substitute or combustion supplement. In these applications, the specification for the purity of DME has been reported to lower than the 99 weight percent (wt%) requirement for current uses, which may provide an opportunity for savings in capital and operating costs for product distillation. If these markets are developed, production capacity for DME will need to increase by an order of magnitude over current levels of about 143,000 metric tons per year. Projects to meet this future market are under development, including two large natural gas-based opportunities serving markets in India and Japan and a coal-based opportunity in China.

## **1. Introduction**

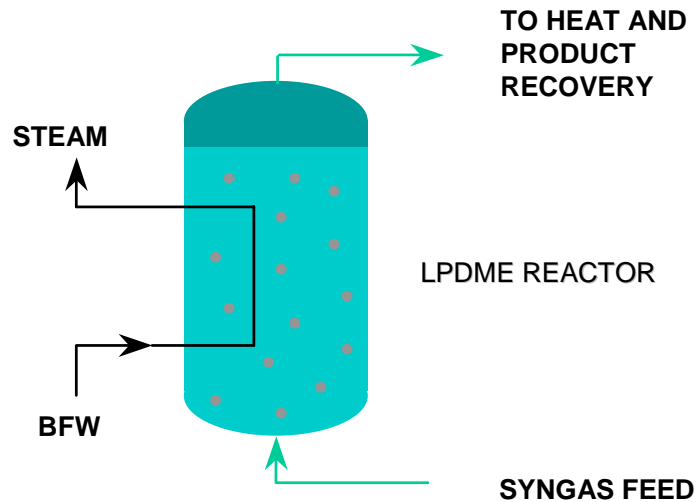
The Liquid Phase Methanol (LPMEOH™) Demonstration Project at Kingsport, Tennessee, is a \$213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L.P., a partnership between Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman), to produce methanol from coal-derived synthesis gas (syngas). Construction of the LPMEOH™ Process Demonstration Facility at Eastman's chemicals-from-coal complex in Kingsport was completed in January 1997. Following commissioning and shakedown activities, the first production of methanol from the facility occurred on 02 April 1997. Nameplate capacity of 260 short tons per day (sT/D) was achieved on 06 April 1997, and production rates have exceeded 300 sT/D of methanol during test periods. Since startup, overall availability has exceeded 98.5%. Eastman has accepted all of the greater than 80 million gallons of methanol produced to date at the LPMEOH™ Demonstration Facility for use in downstream chemical processes.

Sponsored under the DOE's Clean Coal Technology Program, the LPMEOH™ Demonstration Project culminates an extensive cooperative development effort by Air Products and DOE in a program that began in 1981. By the late 1980s, the technology was proven in over 7,400 hours of test operation at a 10-sT/D rate in the DOE-owned Alternative Fuels Development Unit (AFDU) in LaPorte, Texas. Developed to enhance electric power generation using integrated gasification combined cycle (IGCC) technology, the LPMEOH™ Process exhibits several features essential for the economic coproduction of methanol and electricity in the IGCC scenario.

This project has also been evaluating the demonstration of the production of dimethyl ether (DME) as a mixed coproduct with methanol. DME is primarily used as an aerosol propellant, has potential applications as a diesel fuel substitute or combustion supplement, domestic fuel, or chemical building block.

The Air Products' Liquid Phase Dimethyl Ether (LPDME) Process uses a physical mixture of a commercial methanol catalyst and a commercial dehydration catalyst in a single slurry reactor to coproduce DME with methanol (Figure 1). This process provides high syngas conversion, efficient heat transfer, and directly converts a variety of feed gas compositions. Fine catalyst particles are entrained in an inert hydrocarbon liquid, usually a mineral oil. The mineral oil acts as a temperature moderator and a heat removal medium, transferring the heat of reaction from the catalyst surface via the liquid slurry to boiling water in an internal tubular heat exchanger. As a result of this capability to remove heat and maintain a constant, highly uniform temperature

**Figure 1**  
**LPDME Reactor Schematic**



through the entire length of the reactor, the slurry reactor can manage the high syngas conversion per pass that be achieved in the LPDME Process.

In addition, the LPDME Process is particularly well suited to coal-derived syngas which is rich in carbon monoxide. These capabilities make the LPDME Process a potentially lower-cost conversion route to DME, especially when DME coproduction is added to a coal-based IGCC power plant. Syngas mixtures produced from coal as well as natural gas can be converted to form DME.

An excerpt from Commercialization Objectives from the LPMEOH™ Demonstration Project Statement of Work is included here to provide the global perspective regarding the demonstration of the coproduction of DME with methanol:

”Secondary Objective

A secondary objective of the Project is to demonstrate the production of DME (Dimethyl ether) as a mixed coproduct with methanol...

Subject to Design Verification Testing (DVT), the Partnership proposes to enhance the Project by including the demonstration of the slurry reactor's capability to produce DME as a mixed coproduct with methanol...

DVT is required to address issues such as catalyst activity and stability and to provide data for engineering design and demonstration decision making...

At the conclusion of the DVT Steps, a joint Partnership/DOE decision will be made regarding continuation of the methanol/DME demonstration. Timing of the final decision must ensure that



the necessary design, procurement, construction and commissioning can be completed to allow for (Phase 3, Task 2.2) operation at the end of the primary LPMEOH™ process demonstration period."

The first decision milestone, on whether to continue with DVT activities, was targeted for 01 December 1996. This milestone was relaxed to July of 1997 to allow time for further development of the LPDME catalyst system. DVT was considered necessary to provide additional data for engineering design and demonstration decision-making. The essential steps required for decision-making were: a) confirm catalyst activity and stability in the laboratory, b) develop engineering data in the laboratory, and c) confirm market(s), including fuels and chemical feedstocks.

DOE issued a letter dated 31 July 1997 accepting Air Products' recommendation to continue with the design verification testing to coproduce DME with methanol, and to proceed with planning a design verification test run at the LaPorte AFDU. A copy of the recommendation (dated 30 June 1997) is included in the Appendix. The recommendation was based on the results of the Market Economic Studies and on the LPDME catalyst system development work.

The Market Economic Studies show that the LPDME Process should have a significant economic advantage for the coproduction of DME with methanol for local markets. The studies showed that the market applications for DME are large. DME is already being tested as an ultra clean diesel fuel, and is also under evaluation as a clean-burning additive to conventional diesel. DME has been a key intermediate in a commercial syngas-to-gasoline process, and is being developed as an intermediate for other chemicals and fuels.

The 1997 DME DVT recommendation summarizes the catalyst targets, experimental results, and the corresponding economics for a commercially successful LPDME catalyst.

Work on the feasibility study for the coproduction of DME and methanol with electric power was completed. The product DME would be used as a domestic liquid cooking fuel, to replace imported liquid petroleum gas (LPG), for China and the Pacific Rim regions. The results are included in the 1997 DME recommendation in the Appendix.

As part of this activity, a run was conducted in 1999 to coproduce DME with methanol at the LaPorte AFDU and evaluate the commercial viability of the LPDME Process. The results from this operating campaign are presented in a separate Topical Report (Reference 1).

This Topical Report provides data on the status of the current market for DME and an outlook on potential market developments through 2006.

## **2. Results and Discussion**

DME is a colorless and combustible gas at ambient temperature and pressure. As noted above, DME has physical properties that are similar to LPG, and can be stored and transported as a liquid product in pressurized vessels.

The most important application for DME today is as an aerosol propellant. It takes the place of chlorofluorocarbons that have been eliminated due to their harmful effect on the Earth's ozone layer. DME is also an excellent methylating agent for the production of dimethyl sulfate, polyalkylbenzene, and high purity N,N-dimethylaniline, as well as many other chemicals. Given that DME is miscible with many resins and solvents, it is now being used as a cleaning material for laboratory systems and some high precision, high value added cleaning applications, such as in electronics. According to data published by DuPont Company (Reference 2), the following are the uses for DME supplied by DuPont (Table 1):

**Table 1**  
**Applications of DME** (source: DuPont Company)

Uses of DME	Market Share
Hair Spray	48%
Spray Paints/Venturi Sprays	6%
Inspect Repellants/Insecticides	6%
Adhesives	5%
Industrial Feedstocks	31%
Miscellaneous	4%

DME is sold and marketed similarly to LPG. DME is sold by the major producers on a wholesale basis to major users, who store and use the chemical on site. Given the fractionated nature of a large segment of the DME market, over 30% of the DME that is marketed in the United States is sold through distributors, who supply small quantities of DME in either high pressure gaseous cylinders or lower pressure liquid containers to small volume users.

Since the characteristics of DME are similar to those of LPG and given its higher heating value, it has been speculated that DME could be used in large scale power production, in home heating, in replacement of LPG for clean combustion automobiles, and as a diesel fuel substitute or combustion supplement. The latter application is currently being tested in the operation of an on-campus shuttle bus at the Pennsylvania State University, under sponsorship by Air Products, DOE, and the Pennsylvania Department of Environmental Protection (Reference 3).

## **2.1 Current Production/Demand Summary**

The total production of DME today is between 100,000 and 150,000 metric tons per year; a list of the producers is provided in Table 2. In most of these locations, the purity of the DME product is in excess of 99 wt% in order to meet the fitness-for-use requirement for the various applications. One large supplier, with various smaller suppliers servicing regional demands, dominates the market for DME. European nations now produce the majority of DME, with a percentage of that production exported to the United States. Given that DME is only produced in small quantities, the price is very high (about \$3.00 per pound of DME) in relation to the prices for various other sources of energy (an equivalent of about \$0.50 per pound of DME).

**Table 2**  
**World DME Production Capacity (2001)**

<b>Name of Unit</b>	<b>Capacity (Metric Tons per Year)</b>
Shell/RWE (Germany)	60,000
Hamburg DME Co, Germany	10,000
Arkosue Co, Holland	10,000
DuPont, West Virginia	15,000
Australia (various)	10,000
Taiwan (various)	15,000
Japan (various)	10,000
China (various)	13,000
Total Production	143,000

## **2.2 Outlook for Projects (2002-2006)**

The future development of the market for DME as a fuel for power production or automotive transportation will require much larger quantities of DME at a much lower cost. Currently, two projects are known to be pursuing the large-scale production of DME from low cost natural gas feedstocks:

- 1) BP is leading a consortium of companies evaluating the production of DME for use as a fuel to gas turbines in India. Seven Memoranda of Understanding have been signed with customers in South India representing about 2,500 MW capacity. This corresponds to a DME consumption of 4.8 million metric tons per year. The initial plant under development has a production capacity of 5,000 metric tons per day, which exceeds the current worldwide consumption by an order of magnitude; this facility has a reported on-stream date of 2005. When used as a fuel, DME does not need to approach the purity that is required for the current major uses; BP has reported that the DME content in the fuel can vary from 88.0 to 89.8 wt%. This relaxed specification may provide an opportunity for savings in capital and operating costs for product distillation (Reference 4).
- 2) Mitsubishi Gas Chemical Company is considering the development of a project with a similar production rate to the BP project at a location in Western Australia. The plant size under consideration is up to 4,000 to 7,000 metric tons per day of DME. The DME will be used as a fuel for power stations in Japan. Construction is expected to be completed at the end of 2006 pending completion of the necessary approvals.

These projects are now in the stage of development that will require long-term contracts for produced quantities of DME to be used for power production or other large-scale fuel demands.

One project is under development for the production of DME from coal in China. The Ningxia Hui Autonomous Region has announced that a coal gasification facility to produce 830,000 metric tons per year of DME is under evaluation (Reference 5). The potential market for DME

as a household fuel in China has been developed by representatives from the Institute of Coal Chemistry of the Chinese Academy of Sciences in Shanxi. Of the 1.2 billion people in China, 0.3 billion live in cities. Of these, 1/3 currently uses natural gas or LPG. Assuming 4 people per family, the 0.2 billion people who do not use natural gas or LPG converts to 50 million families. If DME captures 20-30% of the market share for these new applications, and the DME consumption is 200 kilograms per family per year, the demand for DME would be 2.4 to 3.0 million metric tons per year.

Additional information on the potential uses for DME can be found through the International DME Association (IDA) (Reference 6). IDA is a non-profit organization that was founded early in 2001 to promote the public awareness and use of DME, to provide a central source of information for all parties interested in DME, and to actively seek opportunities to introduce DME into applications where it will be beneficial to the environment and the economy.

### **3. Conclusions**

This Topical Report provides data on the status of the current market for DME and an outlook on potential market developments through 2006. DME is a colorless and combustible gas at ambient temperature and pressure. DME has physical properties that are similar to LPG, and can be stored and transported as a liquid product in pressurized vessels.

The most important application for DME today is as an aerosol propellant. Over 50% of the demand for DME worldwide (currently between 100,000 and 150,000 metric tons per year) is for this application. DME is also being used as a cleaning material for laboratory systems and some high precision, high value added cleaning applications, such as in electronics. The balance of DME demand is for use as a methylating agent and for miscellaneous experimental work.

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#### **4. References**

1. "Liquid Phase Dimethyl Ether Demonstration in the LaPorte Alternative Fuels Development Unit," DOE Topical Report, Cooperative Agreement No. DE-FC22-92PC90543, January 2001.
2. "Human Health and Environmental Analysis of Dimethyl Ether (DME)," DuPont Company, 22 January 2002, located at [www.chemicalawareness.org/toolkit/nontechnical\\_chem\\_x.pdf](http://www.chemicalawareness.org/toolkit/nontechnical_chem_x.pdf).
3. "Penn State Researchers Investigate Alternative Diesel Fuel," Penn State News, 27 August 2001, located at [www.psu.edu/ur/2001/dme.html](http://www.psu.edu/ur/2001/dme.html).
4. Website for India DME Project ([www.dmeformpower.net/pg\\_background.html](http://www.dmeformpower.net/pg_background.html)).
5. "Promising Coal Chemical Industry in China," China Chemical Reporter, 17 June 2001.
6. Website for International DME Association ([www.aboutdme.org](http://www.aboutdme.org)).

**APPENDIX - JULY 1997 DME DESIGN VERIFICATION TESTING  
RECOMMENDATION**

## **Summary**

From the Statement of Work, "Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process," selected under Round 3 of the U.S. Department of Energy's (DOE's) Clean Coal Technology (CCT) Program: "Subject to Design Verification Testing (DVT), the Partnership proposes to enhance the Project by including the demonstration of the slurry reactor's capability to produce DME (*dimethyl ether*) as a mixed coproduct with methanol." The first DVT step (Phase 1, Task 5), to address issues such as catalyst activity and stability, to provide data for engineering design, and to verify the market through engine tests and through market and economic study, is now complete. The market potential for DME is large, and progress in the laboratory toward developing a catalyst system whose performance meets the economic targets of a methanol equivalent productivity of 14 mol/kg catalyst-hr after 6 months of operation, producing at least 75% (by heating value) DME and 25% methanol.

A test of the Liquid Phase Dimethyl Ether (LPDME) at the LaPorte Alternative Fuels Development Unit (AFDU), in conjunction with the DOE's Liquid Fuels Program, would be appropriate if the catalyst system development can be completed successfully. An implementation decision, made mutually by the DOE's Clean Coal Technology LPMEOH™ project participants, and by the DOE's Liquid Fuels Program participants, should be made (by July of 1997) to implement testing at LaPorte in early 1998. (*Final dates should be recommended by the DOE's Liquid Fuels Program, based on progress in developing the LPDME catalyst system*).

## **Liquid Phase Dimethyl Ether (LPDME) Design Verification Testing (DVT)**

From the Statement of Work, DOE's CCT LPMEOH™ project (Cooperative Agreement No. DE-FC22-92PC90543): "Subject to Design Verification Testing (DVT), the Partnership proposes to enhance the Project by including the demonstration of the slurry reactor's capability to produce DME as a mixed coproduct with methanol. The production of DME from synthesis gas is a natural extension of the LPMEOH™ process in that three reactions occur concurrently in a single liquid phase reactor, methanol synthesis, methanol dehydration and water-gas shift. This process enhancement can significantly improve the overall conversion of coal derived synthesis gas to a storable blend of methanol and DME. -- -- -- the enhanced (DME production demonstration is complementary to ongoing studies being sponsored by DOE's Liquid Fuels Program --) -- . -- At the conclusion of each of the DVT steps, a joint Partnership/DOE decision will be made regarding continuation of methanol/DME demonstration.."

The first DVT step (Phase 1, Task 5), to address issues such as catalyst activity and stability, to provide data for engineering design, and to verify the market through engine tests and through market and economic study, is now complete.

### **The LPDME Process Concept: - Three Concurrent Reactions:**

- $2 \text{ CO} + 4 \text{ H}_2 = 2 \text{ CH}_3\text{OH}$  (Methanol Synthesis).
- $2 \text{ CH}_3\text{OH} = 1 \text{ CH}_3\text{-O-CH}_3 + 1 \text{ H}_2\text{O}$  (Methanol Dehydration).
- $1 \text{ CO} + 1 \text{ H}_2\text{O} = 1 \text{ CO}_2 + 1 \text{ H}_2$  (Water-gas Shift).

The overall reaction, with carbon monoxide (CO)-rich synthesis gas (syngas), in a single liquid phase (slurry) reactor:

- $3 \text{ CO} + 3 \text{ H}_2 = 1 \text{ CH}_3\text{-O-CH}_3 + 1 \text{ CO}_2$  (DME from CO-rich syngas)

This is the "once-through" CO-rich syngas concept for the LPDME process utilizing a single slurry reactor.

Conversion per pass, with CO-rich syngas, can be higher than for the LPMEOH<sup>TM</sup> process. Methanol may also be produced, as a mixed coproduct with the DME, and can easily be separated and recovered. The separation of DME from carbon dioxide (CO<sub>2</sub>) will be necessary for certain market applications.

### **Status of the LPDME DVT Work**

The status of **a)** the LPDME process economics/market study work, and of **b)** the LPDME catalyst system R&D work, follows:

#### **A-1. The market applications** for DME are extensive. DME is, or may be, used as:

- Aerosol - Small, but established market. High purity DME is required.
- Cooking Fuel - Potentially a large market, to replace imported liquefied petroleum gas (LPG).

There is a lot of interest in China, and DME is on the agenda for DOE's Pittsburgh Coal Conference in China (Sept. of 1997). Purity, of about >95% DME, with <2% methanol, < 3% CO<sub>2</sub> is estimated. An unresolved application issue is CO emissions during cooking. How does DME purity impact this? Use testing is needed.

Our contacts with representatives from the Institute of Coal Chemistry of the Chinese Academy of Sciences in Shanxi has provided the following assessment of the potential market for DME as a cooking fuel:

Of the 1.2 billion people in China, 0.3 billion live in cities. Of these, 1/3 currently use natural gas or LPG. Assuming 4 people per family, the 0.2 billion people who do not use gas or LPG converts to 50 million families. If DME captures 20-30% of the market share for these new applications, and the DME consumption is 200 kg per family per year, the demand for DME would be 2.4-3.0 million tons per year.



- Diesel Replacement Fuel. DME is an ultra clean (high Cetane) diesel fuel; and an 80% DME mixture with methanol and water is now being engine-tested by others (Amoco, et. al.). Market development (at least in the U.S.) faces a fuel distribution infrastructure problem. DME might more easily replace LPG in countries where LPG is already an engine fuel. Diesel use in the U.S. is projected to increase by 1.5 percent a year, assuming an economic growth of 1.9 percent a year. This will raise consumption from over 4 quadrillion BTU to approaching 6 quadrillion BTU (Reference 1). This corresponds to an annual increase of almost 1.4 million gallons per year of diesel consumption.
- DME Derivatives, as a Diesel Fuel Additive. Quotes from the DOE Liquid Fuels Program (Contract No. DE-FC22-95PC93052) quarterly report for April-June 1996: "Initial Cetane number (CN) testing of a three-component composition of 1,2-dimethoxy ethane, 1,1-dimethoxy methane and methanol blended with diesel fuel showed a 40% increase in the CN of the diesel fuel when the blend was 50/50." "The concept of adding a blend of oxygenated compounds to diesel fuel in order to enhance the Cetane value and cold start properties is being investigated. The blend of oxygenated compounds is derived from dimethyl ether chemistry, and builds on work conducted earlier --." The testing of this DME feedstock chemistry is in its early days, but it is possible that CO<sub>2</sub> may not need to be separated from the DME prior to the production of DME derivatives. The 50/50 blend referenced above would therefore provide a large market opportunity for the projected U.S. market growth (Reference 1), let alone for the present consumption.
- DME Derivatives, as Chemicals/Other Fuels. DME is a key intermediate in a commercial synthesis gas-to-gasoline process, and is being developed as an intermediate for other chemicals and fuels as part of the DOE's Liquid Fuels Program. The fit for DME here is long-term.

**A-2. The economics studies**, for once-through coproduction (with an integrated gasification combined cycle (IGCC) power plant, for example) on synthesis gas rich in carbon oxides, show that the LPDME process will have an economic advantage greater than the LPMEOH<sup>TM</sup> process. A once-through LPDME reactor is able to convert greater than 50% of such a syngas, whereas a once-through LPMEOH<sup>TM</sup> reactor can convert only about 30%. The economics, of course, depend upon the end-use (purity) of the DME and upon the gasification plant's coproduct mix (amount of power, methanol, DME, etc.). The same liquid phase reactor design options to increase syngas conversion (Reference 2); such as feed gas compression and/or CO-rich gas recycle; are also applicable for LPDME. So, the LPDME technology has the potential to improve on the 5-10 cents per gallon (methanol equivalent) advantage over the LPMEOH<sup>TM</sup> process for the coproduction of DME to serve local markets.

As with the LPMEOH<sup>TM</sup> process, gas phase process technology must be considered as the economic competitor. The gas phase DME process (Reference 3) must run with hydrogen (H<sub>2</sub>)-rich syngas. In the IGCC coproduction flow sheet (shown in Figure 1), gas phase technology is at an economic disadvantage, since separate shift and CO<sub>2</sub>

removal are required. As is the case for methanol, inexpensive remote natural gas would therefore be the economic plant site choice for gas phase technology. A comparison, of IGCC/LPDME coproduction with DME imported from remote gas facilities, shows an advantage of 20-30% for locally produced DME relative to imported DME. The transportation cost to import DME is much higher than for methanol, and the LPDME coproduction advantage is even greater than that for LPMEOH™ (vs. methanol import) (Reference 2). Dehydration of imported methanol to make DME is not competitive either. Therefore, for DME in local markets, LPDME coproduction should be a winner!

With H<sub>2</sub>-rich syngas, the LPDME process loses its (once-through, high conversion per pass) economic advantage. The overall reaction, with (> 2:1) H<sub>2</sub>-rich syngas is:



Since water inhibits the methanol dehydration reaction, the slurry reactor must be staged, with water removal between stages. Staging could be by high ratio gas recycle, and/or with multiple reactors; but the once-through simplicity is lost. Therefore, it is unlikely that the LPDME process would be developed for use in H<sub>2</sub>-rich syngas applications.

A cost estimate of commercial-scale LPDME plants has been performed. This work has helped quantify the targets for the laboratory R&D program (summarized in Part B). From these studies, a commercially successful LPDME system is defined for a Texaco-type synthesis gas (35 mol% H<sub>2</sub>, 51 mol% CO, 13 mol% CO<sub>2</sub>) available at 500 PSIG. At a reactor operating pressure of 950 PSIG and a space velocity of 4,000 liters/hr-kg catalyst, the LPDME catalyst system must have a methanol equivalent productivity of 14 mol/kg catalyst-hr after 6 months of operation, producing at least 75% (by heating value) DME and 25% methanol. Figure 2 shows the effect of plant size on DME cost. These costs are competitive with LPG in China (Section A-1).

## **B. Laboratory R&D Results**

Summary of work through end of funding by CCT LPMEOH™ Project (9/96): An LPDME catalyst system, with reasonable long-term activity (57% of initial activity after 1000 hours), productivity (equivalent methanol productivity of 29 mol/kg catalyst-hr), and selectivity (79% carbon selectivity to DME, CO<sub>2</sub>-free basis), was identified and tested. The system exhibits best activity under CO-rich syngas conditions, i.e. those most likely for (IGCC) coproduction. Accelerated aging of the catalyst system is a remaining issue. Water concentrations in the liquid phase reactor are higher with syngases richer in H<sub>2</sub>, and its effect needs to be evaluated.

Laboratory work has continued under the DOE's Liquid Fuels Program. The issues, to be addressed in the lab before a decision on a test run at the DOE's AFDU in LaPorte, are:

- 1) Understanding the LPDME catalyst system's accelerated aging; and modifying the catalyst and/or the system operating conditions; and
- 2) Manufacturing scale-up of catalyst for a LaPorte AFDU run.

Progress has been made in the laboratory effort. Figure 3 shows the performance for the first DME catalyst which was tested; goals from the Liquid Fuels Program are provided for reference. After further study, an improved DME catalyst (AB-05) was tested with two LPMEOH™ catalysts (S3-86 and MK-101); the results of a 700 hour life study are presented in Figure 4. When compared with the program goals (summarized in Figure 5), the catalyst performance of the newer catalyst is approaching the commercial targets defined in Section A. The status of the laboratory program is summarized in the following table:

	<b>Liquid Fuels Program Goals</b>	<b>Commercial Targets</b>	<b>Laboratory Results</b>
<b>Catalyst Productivity, mol/kg catalyst-hr (MeOH- equivalent)</b>	> 28 (Initial Productivity)	> 14 (productivity for aged catalyst)	28 (Initial Productivity)
<b>Catalyst Selectivity</b>	DME Selectivity > 80% (% Carbon, CO <sub>2</sub> -free)	DME = 75%, Methanol = 25% (heating value basis)	DME Selectivity = 79% (% Carbon, CO <sub>2</sub> -free)
<b>Catalyst Life</b>	> 50% Remaining Activity after 1000 hours	Target Productivity after 6 months of operation	57% Remaining Activity after 1000 hours

Initial discussions with catalyst manufacturers have been held. Once a manufacturer is selected, a laboratory-scale catalyst batch will be produced and tested in the autoclave to verify the production technique developed at Air Products. An interim 1 lb batch will then be produced and tested. Once the catalyst production techniques have been verified at this scale, the 200 lb LaPorte batch will be produced using the same methodology as for a full commercial batch. An autoclave check of this material will be performed prior to the start of the LaPorte AFDU run.

## **Recommendations**

The catalyst system and the market applications/opportunities are sufficiently promising that proof-of-concept testing at the LaPorte AFDU is recommended. Kingsport is an unlikely site for the commercial size demonstration of LPDME, since there are limited times for CO-rich syngas testing; and H<sub>2</sub>-rich syngas would create water buildup. Therefore, the basis for commercializing LPDME must come from:

- 1) catalyst performance (productivity, selectivity, and life) for the LPDME catalyst system under CO-rich syngas from the proof-of-concept testing at the LaPorte AFDU;
- 2) continuing work in hydrodynamics of slurry reactors (other ongoing DOE programs); and
- 3) reactor performance (methanol catalyst activity and life, hydrodynamics, and heat transfer) from the LPMEOH<sup>TM</sup> Process Demonstration Unit.

The tie-in between the laboratory and the LaPorte AFDU is important. Historically, the rate of deactivation of methanol synthesis catalyst has been greater in the autoclave than at the AFDU; this may be a result of loss of catalyst from the autoclave, or due to greater carbonyl poisoning as a result of the higher surface-to-volume ratio at the laboratory scale. Testing at the engineering scale of the LaPorte AFDU can eliminate this variable. Operation of the LPMEOH<sup>TM</sup> Process Demonstration Unit will provide data on catalyst life under coal-derived syngas and at the larger engineering scale (the tie-in to the LaPorte AFDU for commercialization).

The recommendations for proceeding with DVT of the LPDME catalyst system are:

- An LPDME test run at the LaPorte AFDU, in conjunction with the DOE's Liquid Fuels Program, would be appropriate if the LPDME catalyst system development can be completed successfully. Up to \$875,000 of CCT LPMEOH<sup>TM</sup> Project budget support, from the Cost Plan (22 October 1996), should be made available to support a suitable LPDME test run at LaPorte.
- An implementation decision, made mutually by the DOE's CCT (DE-FC22-92PC90543) LPMEOH<sup>TM</sup> Project participants, and by the DOE's Liquid Fuels (DE-FC22-95PC93052) Program participants, should be made (by July of 1997) in time to implement testing at LaPorte in early 1998. (*Final dates should be recommended by the DOE's Liquid Fuels Program, based on progress in developing the LPDME catalyst system*). The CCT LPMEOH<sup>TM</sup> Project participants shall be kept informed (via review meetings and status reports) by Air Products of the development by the DOE Liquid Fuels Program participants of the LaPorte AFDU LPDME test-run plans, so that a timely final approval can be made
- In the interim, some DME product-use testing may be appropriate for the LPMEOH<sup>TM</sup> Demonstration Project's off-site product-use testing.

The schedule for the proposed LPDME testing at the LaPorte AFDU and possible implementation at the Kingsport LPMEOH<sup>TM</sup> Process Demonstration Facility is summarized below:

DME DVT Decision Made	July 1997
Commercial-Scale DME Catalyst Produced/Tested in	
Laboratory Autoclave	January 1998
LaPorte AFDU Test	February/March 1998
Kingsport Decision Made	March/April 1998
Kingsport Implementation (Provisional) Plan	July 1998 - March 2001

### **Impact on CCT Project**

**Technical:** The commercialization of the LPDME Process can be successfully achieved by the combination of the activities at the LaPorte AFDU and the LPMEOH<sup>TM</sup> Process Demonstration Unit described previously.

**Cost:** Up to \$875,000 of Project funds would be available to support a suitable LPDME run. An update of the CCT Project's Cost Plan (22 October 1996), based upon the DVT Recommendation, will be performed following the joint Partnership/DOE decision.

**Schedule:** If the DVT Recommendation is approved by the Partnership and DOE, the operating schedule for the LPMEOH<sup>TM</sup> Process Demonstration Unit will remain unchanged from the current Demonstration Test Plan (September 1996). The DVT would proceed according to the September 1996 DME Milestone Plan (included in the Demonstration Test Plan) and the schedule of the Liquid Fuels Program.

### **References**

1. **Transportation energy consumption by fuel, 1975, 1995 and 2015: History:** Energy Information Administration, *Short-Term Energy Outlook*, DOE/EIA-0202(96/4Q) (Washington, DC, October 1996), and *State Energy Data Report 1994*, DOE/EIA-0214(93). **Projections:** Table A2. Internet access at <http://www/eia.doe.gov/oiaf/aeo97/figure.html#fig46>.
2. **"Fuel and Power Coproduction** - The Liquid Phase Methanol<sup>TM</sup> Process Demonstration at Kingsport", paper presented at Fifth Annual DOE Clean Coal Technology Conference, Tampa, FL, January 7-9, 1997.
3. Haldor Topsoe AS, "Preparation of Fuel Grade Dimethyl Ether", International Publication Number WO9623755, World International Property Organization, 08 August 1996.

Figure 1  
(NOT AVAILABLE ELECTRONICALLY)

Figure 2  
(NOT AVAILABLE ELECTRONICALLY)

Figure 3  
(NOT AVAILABLE ELECTRONICALLY)



Figure 4  
(NOT AVAILABLE ELECTRONICALLY)

Figure 5  
(NOT AVAILABLE ELECTRONICALLY)